



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B41M 1/26, 5/00, D21H 17/54, 19/62, 21/16, C08L 79/00, C08G 73/00	A1	(11) International Publication Number: WO 99/54144 (43) International Publication Date: 28 October 1999 (28.10.99)												
(21) International Application Number: PCT/US99/08911 (22) International Filing Date: 22 April 1999 (22.04.99) (30) Priority Data: <table border="0" style="width: 100%;"><tr><td style="width: 30%;">60/082,697</td><td style="width: 40%;">22 April 1998 (22.04.98)</td><td style="width: 30%;">US</td></tr><tr><td>09/282,595</td><td>31 March 1999 (31.03.99)</td><td>US</td></tr><tr><td>09/282,537</td><td>31 March 1999 (31.03.99)</td><td>US</td></tr><tr><td>09/282,542</td><td>31 March 1999 (31.03.99)</td><td>US</td></tr></table> (71) Applicant: SRI INTERNATIONAL [US/US]; 333 Ravenswood Avenue, Menlo Park, CA 94025 (US). (72) Inventor: NIGAM, Asutosh; 4506 Amiens Avenue, Fremont, CA 94555 (US). (74) Agents: REED, Dianne, E.; Reed & Associates, 3282 Alpine Road, Portola Valley, CA 94028 (US) et al.		60/082,697	22 April 1998 (22.04.98)	US	09/282,595	31 March 1999 (31.03.99)	US	09/282,537	31 March 1999 (31.03.99)	US	09/282,542	31 March 1999 (31.03.99)	US	(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
60/082,697	22 April 1998 (22.04.98)	US												
09/282,595	31 March 1999 (31.03.99)	US												
09/282,537	31 March 1999 (31.03.99)	US												
09/282,542	31 March 1999 (31.03.99)	US												
(54) Title: TREATMENT OF SUBSTRATES TO ENHANCE THE QUALITY OF PRINTED IMAGES THEREON USING AZETIDINIUM AND/OR GUANIDINE POLYMERS (57) Abstract <p>Compositions and methods are provided for improving the quality of images printed on a substrate. The image-enhancing compositions contain as an image-enhancing agent (a) an azetidinium polymer, (b) a guanidine polymer, (c) a mixture of an azetidinium polymer and a guanidine polymer, or (d) a copolymer of an azetidinium monomer and a guanidine monomer. When applied to a substrate, the compositions provide for high quality printed images when the treated substrate is printed on with an ink containing a reactive dye capable of reacting with the image-enhancing agent. Images printed on a substrate treated with the image-enhancing compositions of the invention are water-resistant (e.g., water-fast), bleed-resistant, rub-resistant, and/or are characterized by an enhanced chroma and hue.</p>														

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TREATMENT OF SUBSTRATES TO ENHANCE THE
QUALITY OF PRINTED IMAGES THEREON
USING AZETIDINIUM AND/OR GUANIDINE POLYMERS

5

TECHNICAL FIELD

The present invention relates generally to compositions and methods for the treatment of substrates, and more particularly relates to compositions and methods for treating substrates to enhance the quality of images printed thereon. The invention is useful in the treatment of a wide variety of substrate types, including flexible and rigid substrates, porous and nonporous substrates, cellulosic and noncellulosic substrates, and the like.

BACKGROUND ART

As printing technology advances, manufacturers of many different types of products are faced with the increasingly rigorous demands of their customers for high quality printed images on those products. Such products include, for example, printed textiles, paper, printed polymeric sheets, coatings or films, printed metallic items, and the like.

For example, current textile printing technologies are deficient in meeting modern, time-driven, demand-responsive manufacturing strategies. In general, the conventional method of printing on textiles involves crosslinking a colorant to the cellulosic fiber of the textile itself. This approach is limited in that it relies on processes that involve multiple, time-consuming steps. The types of substrates and colorants that can be used are limited as well. One approach for increasing textile printing speed involves the use of inkjet printing. Inkjet printers are very popular, due at least in part to their reliability, relatively quiet operation, versatility, graphics capability, print quality, and low cost. Moreover, inkjet printers have made possible "on demand" color printing without the need for complicated devices. Because inkjet printing has become so popular in both home and commercial use, several water-soluble inks are available. The inks are typically composed of water and a colorant, usually a dye or pigment dispersion, and often contain a number of

additives for imparting certain features to the ink (e.g., improved stability and flow, smear resistance, and the like). Unfortunately, however, using inkjet printing techniques for printing on textiles has met with several problems. First, and in spite of the large number of inkjet inks currently available, inkjet printed images on textiles are often of low quality.

5 For example, the printed images often smear upon handling, exhibit bleed (the intrusion of one color into an adjacent color), are moisture sensitive, and are dull, *i.e.*, colored inks when printed fail to accurately produce the expected hues. Moreover, the printed images are often neither water-fast nor detergent-resistant, resulting in fading of the printed image after washing. Printed textile images with these drawbacks are wholly unacceptable to the
10 textile industry, which requires not only that the image be both water-resistant and detergent-resistant, but also that the colors and hues are those deemed acceptable in the textile field.

In addition, there is a keen demand for paper that can be printed on to provide images of exceptionally high quality, particularly with respect to brightness, clarity,
15 opacity, water-fastness, water resistance, bleed resistance and rub resistance. The customer further demands that paper be amenable to use with a variety of printing techniques, including not only conventional printing techniques, but also "impact-free" printing techniques such as inkjet printing (particularly colored inkjet printing), laser printing, photocopying, and the like.

20 In response, paper manufacturers have attempted to meet their customers' demands for such high quality paper through a process termed "sizing." "Sizing," which encompasses both "internal sizing" and "external sizing," affects the manner in which colorants and particularly ink interact with the fibers of the paper. "Internal sizing" involves introduction of sizing compositions within the entire fibrous mass at the pulp stage
25 of paper manufacturing (*i.e.*, to the wet pulp, or more specifically, to the prepared papermaking furnish) before the stock is formed into a sheet, resulting in the distribution of the sizing composition within the entire fibrous mass that is subsequently used to produce the flat fibrous paper sheet. "External sizing" (also referred to as surface application, pasting, saturating or coating) involves application of a sizing composition to at least one
30 surface of a fibrous paper sheet, so that the composition is present on or in at least one of

the two faces of the fibrous sheet. Various materials have been used as sizing agents, such as conventional and modified starches, polyvinyl alcohol, cellulosic derivatives, gelatin, rosin, proteins such as casein, natural gums and synthetic polymers. Although these materials are effective to various degrees under certain conditions, use of each is associated with certain limitations. For example, it is often necessary to use large amounts of these conventional sizing agents in order to provide paper having the desired properties. However, the opacity and brightness of the paper substrate decrease in direct proportion to the amount of sizing agent applied to the paper. Moreover, as the amount of sizing agent and/or the cost of the sizing agent increases, the cost of producing the paper increases, making high quality papers prohibitively expensive. Certain sizing agents impart relatively poor bleed resistance and water resistance of imprinted inks, and thus must be used with insolubilizing agents to ensure production of a printed paper having satisfactory water resistance.

Use of conventional sizing agents also results in a decrease in the porosity of the final paper substrate; thus, while the sized paper substrate may have the desired brightness and opacity, it may not provide for a printed image having a suitable optical density or color intensity. In addition, as the porosity of the paper increases, the paper becomes less amenable to various handling processes during manufacturing. For example, envelope manufacturers demand that the paper available to them have a relatively low porosity. If the porosity of the paper is too high, the paper is too stiff for handling by automated industrial devices for folding and sorting (*e.g.*, devices of the "suction extractor" type) during envelope production. In contrast to lower porosity papers, high porosity papers also require slower machine speeds, and further require refining and draining operations that have relatively high energy costs.

Coatings have additionally been used to enhance the quality of printed images on paper, albeit with limited success. Regarding other types of substrates, a variety of coating methods and compositions have also been suggested. However, as with textiles and paper, there is not at this time any satisfactory method for improving the quality of images printed on polymeric films, metallic sheets, or the like using water-based inks.

The present invention is directed to the aforementioned need in the art, and provides an efficient, versatile and cost-effective means for treating substrates that can then be printed on to yield high quality, water-resistant printed images. The compositions and methods of the invention are amenable for use with a wide variety of substrate types, and
5 are compatible with conventional manufacturing and post-manufacturing handling processes.

DISCLOSURE OF THE INVENTION

The present invention features novel image-enhancing compositions for treating a
10 substrate to enhance the quality of images printed thereon, wherein the image-enhancing compositions are composed of an image-enhancing agent selected from one of (a) an azetidinium polymer, (b) a guanidine polymer, (c) a mixture of an azetidinium polymer and a guanidine polymer, and (d) a copolymer of an azetidinium monomer and a guanidine monomer. Substrates can be treated before or during manufacture. Substrates treated with
15 the present image-enhancing compositions can be printed on to yield high quality printed images, particularly when printed on with an ink containing a reactive dye having ionizable and/or nucleophilic groups capable of reacting with the image-enhancing agent. The printed images are bleed-resistant, rub-resistant, water-resistant (*e.g.*, water-fast), and/or are characterized by an enhanced chroma and hue.

20 It is a primary object of the invention to address the above-mentioned need in the art by providing such an image-enhancing composition that efficiently binds colorant upon printing. Another object of the invention is to provide a treated substrate that can be printed on to yield an image that is high quality (particularly with respect to optical density and brightness), and that is bleed-resistant, rub-resistant, and water-resistant (*e.g.*, water-
25 fast).

Still another object of the invention is provide a method for treating substrates using the image-enhancing compositions of the invention.

Still an additional object of the invention is to provide a method for printing on a substrate to provide water-resistant (*e.g.*, water-fast) printed images thereon.

Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention.

5

MODES FOR CARRYING OUT THE INVENTION

DEFINITIONS AND NOMENCLATURE:

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "an image-enhancing agent" in a composition means that more than one image-enhancing agent can be present in the composition, reference to "a polymer" includes combinations of different polymers, and the like.

"Aqueous based ink" refers to an ink composed of an aqueous carrier medium and a colorant, such as a dye or a pigment dispersion. An aqueous carrier medium is composed of water or a mixture of water and one or more water-soluble organic solvents. Exemplary aqueous based ink compositions are described in detail below.

"Colorant" as used herein is meant to encompass dyes, pigments, stains, and the like compatible for use with the image-enhancing compositions of the invention.

The term "colorant-reactive component" as used herein refers to a component (*e.g.*, a chemical moiety) of an image-enhancing agent that is capable of reacting with a selected colorant, particularly a colorant having a nucleophilic and/or ionizable group, to form an image-enhancing agent-colorant complex. The image-enhancing agent-colorant complex is formed through either a covalent, electrostatic, or ionic association between the colorant-reactive component of the image-enhancing agent and the colorant. When an image-enhancing agent having a colorant-reactive component and a selected colorant from an image enhancing agent-colorant complex in the context of a printed image on a substrate, the association between the colorant and the color-reactive component of the image-enhancing agent is effective to impart advantageous qualities to the printed image on

the substrate, particularly with respect to water resistance, enhanced optical density, enhanced brightness, and the like.

The term "treating," as used herein to refer to the application of an image-enhancing composition of the invention to a substrate, is intended to include both
5 application of a coating to a substrate surface as well as partial or complete saturation of a substrate with the composition.

The term "organic solvent" is used herein in its conventional sense to refer to a liquid organic compound, typically a monomeric organic material in the form of a liquid, preferably a relatively nonviscous liquid, the molecular structure of which contains
10 hydrogen atoms, carbon atoms, and optionally other atoms as well, and which is capable of dissolving solids, gases or liquids.

The term "significant", as when used with reference to "significantly enhanced brightness" or "significantly improved water-fastness" generally refers to a difference in a quantifiable, measurable, or otherwise detectable parameter, *e.g.*, optical density, LAB
15 graphs (color sphere), dot spread, bleed through, between the two groups being compared (*e.g.*, untreated versus treated substrates) that is statistically significant using standard statistical tests. For example, the degree of visual wicking or water-fastness of a printed substrate as detected in a print assay may be quantified using standard methods, and the degree of wicking or water-fastness under different conditions can be compared for both
20 treated and untreated substrates to detect statistically significant differences.

The term "fluid resistance" is used herein to describe the resistance of a printed substrate to penetration by a fluid, with the term "water resistance" specifically referring to resistance of a substrate to penetration by water.

The term "water-fast," is used herein to describe a form of water resistance, and
25 which is normally used to refer to the nature of the ink composition after drying on a substrate. In general, "water-fast" means that the dried composition is substantially insoluble in water, such that upon contact with water, the dried ink retains at least about 70%, preferably at least about 85%, and more preferably at least about 95%, of optical density.

The term "bleed resistance" is meant to refer to the retardation of the penetration of water into a substrate, which retardation is associated with creation of a low energy hydrophobic surface at the fiber-water interface which increases the contact angle formed between a drop of liquid and the surface, and thus decreases the wettability. Contact angles have been shown to be sensitive to molecular packing, surface morphology, and chemical constitution of the substrate and any components added thereto.

The term "rub resistance" is normally meant to refer to a characteristic of the ink composition after drying on a substrate, more specifically, the ability of a printed image to remain associated with the substrate upon which it is printed despite application of force (e.g., rubbing) to the printed image. In general, "rub resistant" means that the dried ink composition is substantially resistant to rubbing force so that the dried ink retains at least about 70%, preferably at least about 85%, and more preferably at least about 95%, of optical density after rubbing of the printed image.

The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like, as well as cycloalkyl groups such as cyclopentyl, cyclohexyl and the like. The term "lower alkyl" intends an alkyl group of 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms.

The term "alkylene" as used herein refers to a difunctional, branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, including without limitation methylene, ethylene, ethane-1,1-diyl, propane-2,2-diyl, propane-1,3-diyl, butane-1,3-diyl, and the like. "Lower alkylene" refers to an alkylene group of 1 to 6 carbon atoms.

The term "alkoxy" as used herein intends an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group may be defined as -OR where R is alkyl as defined above. A "lower alkoxy" group intends an alkoxy group containing 1 to 6 carbon atoms.

"Halo" or "halogen" refers to fluoro, chloro, bromo or iodo, and usually relates to halo substitution for a hydrogen atom in an organic compound.

The term "polymer" is used herein in its conventional sense to refer to a compound having two or more monomer units, and is intended to include homopolymers as well as copolymers. The term "monomer" is used herein to refer to compounds which are not polymeric.

5 "Optionally" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not. For example, the phrase "optionally substituted" aromatic ring means that the aromatic ring may or may not be substituted and that the description includes both an unsubstituted aromatic ring and an
10 aromatic ring bearing one or more substituents.

OVERVIEW OF THE INVENTION:

The present invention is based upon the discovery that a composition containing an image-enhancing agent that is one of (a) an azetidinium polymer, (b) a guanidine polymer,
15 (c) a mixture of an azetidinium polymer and a guanidine polymer, and (d) a copolymer of an azetidinium monomer and a guanidine monomer, is effective in treating a wide variety of substrates to significantly improve the quality of images printed thereon. Substrates that have been treated with an image-enhancing composition of the invention can be printed on to yield high quality printed images having improved color fastness (the printed images do not
20 run when exposed to moisture) as a result of the substantially non-reversible binding of aqueous colorants to the image-enhancing agent present in the image-enhancing composition. Substrates that are treated with the compositions of the invention and then printed on thus provide images that can be characterized as "water-resistant" or "water-fast" due to the characteristics of the printed image following exposure to water. The printed images are also
25 bleed-resistant as well as rub-resistant.

The treated substrates of the invention can be used in conventional printing, or with digital printing (particularly inkjet printing, including drop-on-demand and continuous printing) to provide highly brilliant, printed images that are significantly improved in color quality, for example, with respect to chroma and hue, when compared to untreated substrates
30 or conventionally treated substrates. The present compositions and their methods of use

according to the present invention thus provide a number of advantages over conventional textile treatment compositions, paper coating and sizing compositions, and the like.

The image-enhancing compositions, methods of treatment using the image-enhancing compositions described herein, and other features of the invention are described in

5 greater detail below.

IMAGE-ENHANCING COMPOSITIONS:

The image-enhancing compositions of the invention are composed of an image-enhancing agent selected from the group consisting of (a) an azetidinium polymer, (b) a
10 guanidine polymer, (c) a mixture of an azetidinium polymer and a guanidine polymer, and (d) a copolymer of an azetidinium monomer and a guanidine monomer. In general, the image-enhancing agents have a colorant-reactive component that is capable of reacting with a selected colorant, particularly a colorant having a nucleophilic and/or ionizable group, to form an image-enhancing agent-colorant complex through a covalent, electrostatic, or ionic
15 association. The association of the image-enhancing agent and colorant imparts water resistance (*e.g.*, water-fastness) and other desirable characteristics to the printed image on the substrate surface. In addition to the image-enhancing agent, the image-enhancing compositions can include components such as film-forming binders, pigments, and other additives.

20 The image-enhancing compositions of the invention can be readily prepared from commercially available starting materials and/or reagents, are compatible with additional binders or additives, can be used with a variety of substrates, are compatible with a variety of printing methods, including conventional and digital printing methods (particularly inkjet printing, including drop-on-demand printing and continuous printing), and can also be used
25 with existing commercial manufacturing methods and equipment, including, for example, textile and paper production processes and equipment. The image-enhancing composition is inexpensive to prepare, and relatively small amounts are required to provide a treated substrate having the advantageous features described herein. The image-enhancing compositions of the invention are also easy to handle due to their solubility in water (the
30 active components, the image-enhancing agents, are hydrophilic polymers), and do not

require the use of large volumes of organic solvents. The novel image-enhancing compositions herein also possess good film-forming properties.

The treated substrates prepared using the compositions of the invention react rapidly with a number of aqueous based colorants. Furthermore, because colorants react quickly with the image-enhancing agent in the present compositions, the printed-on, treated substrate does not require a separate curing step, but rather is fast-drying. This fast-drying characteristic provides for printed images that are "non-sticky," thus allowing the printed substrate to be handled immediately after printing. In addition to their water resistance, substrates treated with an image-enhancing composition of the invention are highly bleed-resistant (as evidenced by small dot size measurements, *i.e.*, less wicking action) and rub-resistant.

The various components of the image-enhancing composition will now be described.

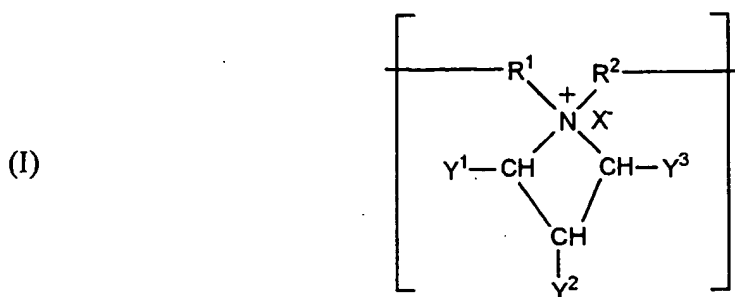
1. IMAGE-ENHANCING AGENTS

Image-enhancing agents in the image-enhancing compositions of the invention generally comprise an azetidinium polymer, a guanidine polymer, a copolymer of an azetidinium monomer and a guanidine monomer, or a mixture of an azetidinium polymer and a guanidine polymer. The image-enhancing agent typically represents approximately 5% to 95% of the image-enhancing composition, preferably approximately 10% to 95% of the image-enhancing composition, based upon total solids weight of the composition after drying.

A) AZETIDINIUM POLYMERS

In one embodiment, the image-enhancing agent is an azetidinium polymer. An "azetidinium polymer" is a polymer comprised of monomeric subunits containing a substituted or unsubstituted azetidine ring (*i.e.*, a four membered nitrogen-containing heterocycle). In general, the azetidinium polymers useful herein are composed of monomer units having the structural formula (I):

-11-

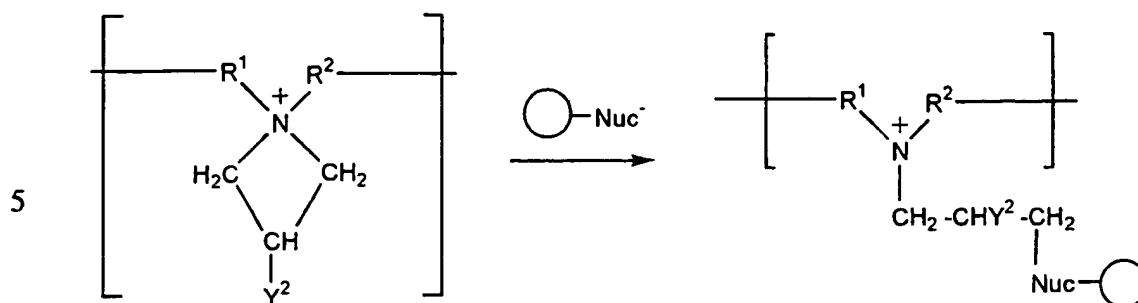


in which R^1 and R^2 are independently lower alkylene, X^- is an anionic, organic or inorganic counterion, and Y^1 , Y^2 and Y^3 are selected from the group consisting of hydrogen, hydroxyl, halo, alkoxy, alkyl, amino, carboxy, acetoxy, cyano and sulfhydryl. Preferred such polymers are wherein R^1 and R^2 are methylene, X^- is selected from the group consisting of halide, acetate, methane sulfonate, succinate, citrate, malonate, fumarate, oxalate and hydrogen sulfate, Y^1 and Y^3 are independently hydrogen or lower alkyl, and Y^2 is hydrogen or hydroxyl. In particularly preferred azetidinium polymers herein, Y^1 and Y^3 are hydrogen and Y^2 is hydroxyl.

The azetidinium polymer may be a homopolymer, or it may be a copolymer, wherein one or more non-azetidinium monomer units are incorporated into polymer structure. Any number of comonomers may be employed to form suitable azetidinium copolymers for use herein; however, a particularly preferred azetidinium copolymer is aminoamide azetidinium. Further, the azetidinium polymer may be essentially straight-chain or it may be branched or crosslinked.

Azetidinium polymers can associate with colorant in two different ways. First, the azetidinium polymer can associate with colorant through an ionic interaction, where the colorant provides anionic groups, such as carboxy or sulfonate, that can ion-exchange with the polymer counterions (X^- in Formula (I), above), thus fixing the colorant to the treated substrate via an electrostatic-type interaction. Second, nucleophilic groups present within the colorant can react with the azetidinium groups of the polymer via a ring-opening reaction. A characteristic ring-opening reaction of an azetidinium polymer of the invention may be illustrated as follows:

-12-

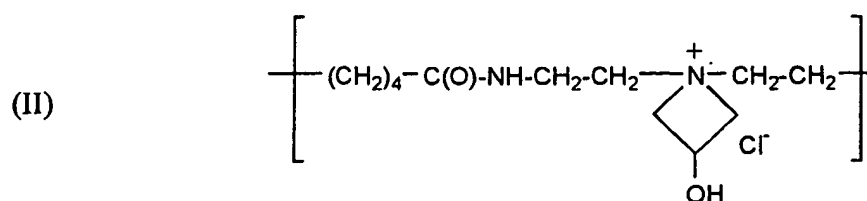


The colorant thus covalently bonds to the azetidinium polymer to form an azetidinium
 10 polymer-colorant complex. Colorant thus applied to a treated substrate is rapidly and
 irreversibly bound to the substrate.

The percentage of reactive azetidinium groups in the polymer can be adjusted in a
 controlled manner. Azetidinium groups are insensitive to pH change; however, such groups
 are highly sensitive to the presence of anionic and nucleophilic species. In some cases, it
 15 may be desirable to adjust the reaction conditions used to prepare the azetidinium polymer
 (e.g., by raising the pH) to generate anionic groups within the polymer, which then
 participate in intramolecular crosslinking.

A preferred azetidinium polymer for use in the present invention is shown in
 Formula (II)

20



25 Commercially available such polymers include "AMRES[®]," available from Georgia Pacific,
 Resins, Inc., Atlanta, GA, "KYMENE[®]," from Hercules, Inc., Wilmington, DE, and
 "Polycup[®]," also from Hercules, Inc. These azetidinium polymers are generally referred to
 as poly(aminoamide)-epichlorohydrin (PAE) resins; such resins are typically prepared by
 alkylating a water-soluble polyamide containing secondary amino groups with
 30 epichlorohydrin. Other suitable azetidinium polymers will be known to those skilled in the

art and/or are described in the pertinent texts, patent documents, and literature references; see, for example, Moyer, *et al.*, in WET STRENGTH IN PAPER AND PAPERBOARD, Tappi Monograph Series No. 29, Tappi Press, Ch. 3, p. 33-37 (1965); Chan, in TAPPI WET AND DRY STRENGTH SHORT COURSE, Tappi Press, Atlanta, April 13-15, 1988; and Espy, in WET STRENGTH RESINS AND THEIR APPLICATION, Ed., Lock L. Chan, Tappi Press, Atlanta, GA (1994).

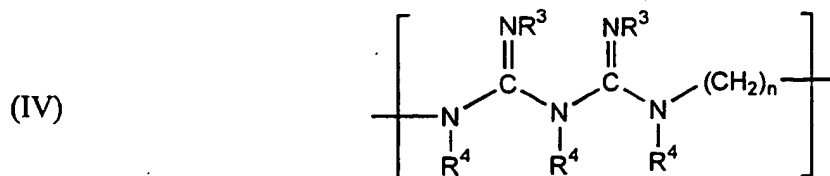
(B) GUANIDINE POLYMERS

In another embodiment, the image-enhancing agent is a guanidine polymer, also termed a "polyguanidine." The guanidino group is extremely basic, possessing a pKa of about 12-13. Polyguanidines for use in the invention are typically provided as acid salts wherein the imine nitrogen atoms are for the most part in protonated form.

In general, guanidine polymers useful as image-enhancing agents in the present invention are either homopolymers or copolymers. All guanidine polymers herein are comprised of recurring monomer units having the structural formula



wherein R³ is hydrogen or lower alkyl and R⁴ is hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy. Preferably, R³ and R⁴ are hydrogen. Particularly preferred guanidine polymers for use herein are comprised of monomer units having the structural formula (IV)



-14-

wherein n is an integer in the range of 1 to 10 inclusive, R^3 is hydrogen or lower alkyl and R^4 is hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy. Preferably, R^3 and R^4 are hydrogen.

5 A particularly preferred guanidine polymer for use in the methods and compositions of the invention has the structure of formula (IV) wherein R^3 and R^4 are H and n is 6 (3,12-diimino-2,4,11,13-tetraazatetradecanediimidamide), available commercially as "BAQUACIL®" and "VANTOCIL®," from Zeneca, Inc.

Guanidine polymers of the invention react electrostatically with anionic groups present in the dye via ion-exchange type interactions, to rapidly and irreversibly bind anionic
10 type dyes to print substrates treated with such polymers.

(C) MIXTURES OF AZETIDINIUM POLYMERS AND GUANIDINE POLYMERS

In another embodiment, the image-enhancing agent comprises a mixture of an azetidinium polymer and a guanidine polymer. The two polymers may be present in any
15 suitable ratio relative to one another. The relative amounts of polyguanidine and polyazetidinium can range from about 0.05% polyguanidine/99.95% polyazetidinium to 0.05% polyazetidinium/99.95% polyguanidine. The actual relative amounts of polyguanidine and polyazetidinium will vary according to the composition of the ink to be used (*e.g.*, the nature of the colorant in the ink), the nature of the substrate, and other factors
20 affecting the use of the polymers, such as the relative market price for each polymer. In general, it is preferable to use a smaller amount of guanidine relative to azetidinium.

In this embodiment, it is important that the pH of the image-enhancing composition be acidic, as the composition tends to gel at basic pH. If necessary, then, an acid should be added to the composition to ensure that the pH is below 7.0, preferably less
25 than about 5.5, and most preferably in the range of about 1.0 to 5.5. Suitable acids include sulfuric acid, hydrochloric acid, acetic acid, and the like.

Although it will be appreciated that any of a number of azetidinium or guanidine polymers can be used to prepare the treated substrates and image-enhancing compositions described herein, a preferred polymer is a poly (aminoamide)-azetidinium polymer, *e.g.*, a

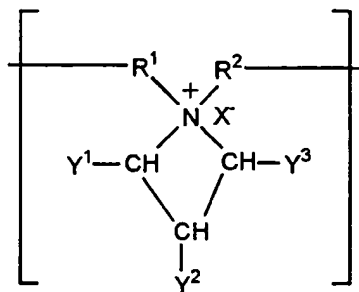
polyazetidinium chloride-based polymer, such as a polyamide-polyamine-epichlorohydrin resin.

(D) COPOLYMERS OF AZETIDINIUM MONOMERS AND GUANIDINE MONOMERS

- 5 In another embodiment, the image-enhancing agent is a copolymer of an azetidinium monomer unit and a guanidine monomer unit. In general, the azetidinium monomer unit has the structural formula (I)

10

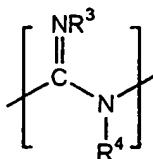
(I)



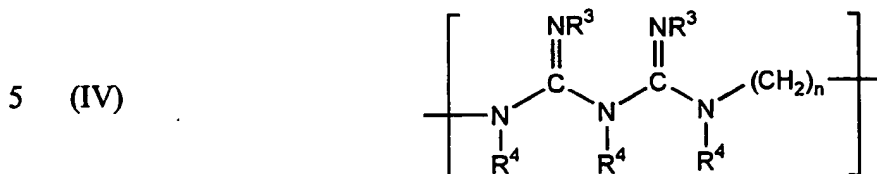
- 15 in which R^1 and R^2 are independently lower alkylene, X^- is an anionic, organic or inorganic counterion, and Y^1 , Y^2 and Y^3 are selected from the group consisting of hydrogen, hydroxyl, halo, alkoxy, alkyl, amino, carboxy, acetoxy, cyano and sulfhydryl. Preferred monomers are wherein R^1 and R^2 are methylene, X^- is selected from the group consisting of halide, acetate, methane sulfonate, succinate, citrate, malonate, fumarate, oxalate and hydrogen sulfate, Y^1 and Y^3 are independently hydrogen or lower alkyl, and Y^2 is hydrogen or hydroxyl. In particularly preferred azetidinium monomers, Y^1 and Y^3 are hydrogen and Y^2 is hydroxyl. The guanidine monomer has the structural formula (III)
- 20

(III)

25



or the structural formula (IV)



wherein R^3 , R^4 and n are as defined earlier herein.

The ratio of azetidinium monomers to guanidine monomers in the copolymer, as well as the distribution of each monomer type in the copolymer, can be varied according to a number of factors, and may be, for example, tailored for use with specific colorants having certain types of ionic and/or nucleophilic groups. The precise composition of the copolymer may also be varied to best accommodate the nature of the substrate to be treated.

15 2. FILM-FORMING BINDERS

The image-enhancing compositions of the invention preferably include a film-forming binder. By "film-forming binder" is meant a substance that provides for improved strength of a substrate upon application of the substance to the substrate. "Film-forming binders" used in connection with the image-enhancing compositions of the invention include any film-forming binder that is compatible with the selected image-enhancing agent and other components of the image-enhancing composition. Exemplary film-forming binders include, but are not necessarily limited to: polysaccharides and derivatives thereof, *e.g.*, starches, cellulosic polymers, dextran and the like; polypeptides (*e.g.*, collagen and gelatin); and synthetic polymers, particularly synthetic vinyl polymers such as poly(vinyl alcohol), poly(vinyl phosphate), poly(vinyl pyrrolidone), vinyl-pyrrolidone-vinyl acetate copolymers, vinyl alcohol-vinyl acetate copolymers, vinyl pyrrolidone-styrene copolymers, and poly(vinyl amine), and cationic film-forming binders such as quaternized vinyl pyrrolidone-dimethylaminoethyl-methacrylate copolymer, dimethylaminoethyl-methacrylate-co-methyl methacrylate, polydiallyldimethyl ammonium chloride and quaternized aminoacrylate polymers.

20
25
30

Polysaccharide binders: Starches, as noted above, represent one category of suitable film-forming binders for use herein. Suitable starches may be any of a variety of natural, converted, and synthetically modified starches. Exemplary starches include, but are not necessarily limited to, starch (*e.g.*, SLS-280 (St. Lawrence Starch)), cationic starches (*e.g.*, Cato-72 (National Starch)), hydroxyalkylstarch, wherein the alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from about 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, or the like (*e.g.*, hydroxypropyl starch #02382 (PolySciences, Inc.), hydroxyethyl starch #06733 (PolySciences, Inc.), Penford Gum 270 and 280 (Penford), and Film-Kote (National Starch)), starch blends (see, *e.g.*, U.S. Pat. No. 4,872,951, describing a blend of cationic starch and starch treated with an alkyl or alkenyl succinic anhydride (ASA), preferably 1-octenyl succinic anhydride (OSA)), and the like. The film-forming binder can also be a synthetically produced polysaccharide, such as a cationic polysaccharide esterified by a dicarboxylic acid anhydride (see, *e.g.*, U.S. Pat. No. 5,647,898). Additional saccharide binders include cellulosic materials such as alkyl celluloses, aryl celluloses, hydroxy alkyl celluloses, alkyl hydroxy alkyl celluloses, hydroxy alkyl celluloses, dihydroxyalkyl cellulose, dihydroxyalkyl cellulose, hydroxy alkyl hydroxy alkyl cellulose, halodeoxycellulose, amino deoxycellulose, dialkylammonium halide hydroxy alkyl cellulose, hydroxyalkyl trialkyl ammonium halide hydroxyalkyl cellulose, dialkyl amino alkyl cellulose, carboxy alkyl cellulose salts, cellulose sulfate salts, carboxyalkylhydroxyalkyl cellulose and the like). Still additional film-forming binders of this type include dextran (*e.g.*, dialkyl aminoalkyl dextran, amino dextran, and the like), carrageenan, Karaya gum, xanthan, guar and guar derivatives, (*e.g.*, carboxyalkyl hydroxyalkyl guar, cationic guar, and the like), and gelatin.

Additional exemplary film-forming binders include resins (*e.g.*, such as formaldehyde resins such as melamine-formaldehyde resin, urea-formaldehyde resin, alkylated urea-formaldehyde resin, and the like), acrylamide-containing polymers (*e.g.*, poly(acrylamide), poly(N,N-dimethyl acrylamide), and the like), poly(alkyleneimine)-containing polymers (*e.g.*, poly(ethyleneimine), poly(ethyleneimine) epichlorohydrin, alkoxylated poly(ethyleneimine), and the like), polyoxyalkylene polymers (*e.g.*, poly(oxymethylene), poly(oxyethylene), ethylene oxide/propylene oxide copolymers,

ethylene oxide/2-hydroxyethyl methacrylate/ethylene oxide and ethylene oxide/hydroxypropyl methacrylate/ethyleneoxide triblock copolymers, ethylene oxide-4-vinyl pyridine/ethylene oxide triblock copolymers, ethylene oxide-isoprene/ethylene oxide triblock copolymers, epichlorohydrin-ethylene oxide copolymer, and the like), *etc.*

5 Any of the above exemplary film-forming binders can be used in any effective relative amounts, although typically the film-forming binder, if present, represents approximately 1 wt.% to 40 wt.%, preferably 1 wt.% to 25 wt.%, most preferably 1 wt.% to 15 wt.% of the present image-enhancing composition, after drying on a substrate. Starches and latexes are of particular interest because of their availability and applicability to a variety
10 of substrates.

3. OTHER COMPONENTS OF THE IMAGE-ENHANCING COMPOSITION

Additional components of the image-enhancing composition may include, but are not necessarily limited to, inorganic fillers, anti-curl agents, surfactants, plasticizers,
15 humectants, UV absorbers, light fastness enhancers, polymeric dispersants, dye mordants, optical brighteners, and leveling agents, as are commonly known in the art. Illustrative examples of such additives are provided in U.S. Patent Nos. 5,279,885 and 5,537,137. The image-enhancing compositions may also include a crosslinking agent such as zirconium acetate, ammonium zirconium carbonate, or the like, for intramolecular and/or
20 intermolecular crosslinking of image-enhancing agent, and/or a chelating agent such as boric acid. Of particular interest with respect to the treatment of paper substrate are components that provide for a coated substrate having a non-glossy, matte, or glossy surface; as will be appreciated by those skilled in the art, incorporation of a pigment (e.g., silica, calcium carbonate) will generally give rise to a non-glossy surface, while a glossy surface will result
25 in the absence of a pigment (or in the presence of only a small amount of pigment).

The image-enhancing composition may also contain a colorant, *e.g.*, a pigment, dye or other colorant, to provide for whiteness or color of the substrate; this is particularly true for use in sizing or coating paper. Additional components that may be desirable to include in the compositions of the invention, particularly when the compositions are to be
30 used to treat paper, are found in PAPER CHEMISTRY, 2nd Edition, Roberts, ed., Blackie

Academic & Professional, Glasgow, UK (1994). The aforementioned reference also provides guidance for the use of such components and a general description of paper chemistry.

The image-enhancing composition of the invention is preferably provided in an aqueous liquid vehicle, although small amounts of a water-soluble organic solvent may be present. The aqueous liquid vehicle will generally be water, although other nonorganic compounds which are either water soluble or water miscible may be included as well. It may on occasion be necessary to add a solubilizing compound during preparation of the image-enhancing composition so that the components dissolve in the aqueous liquid vehicle, *e.g.*, an inorganic base such as ammonia and/or an organic amine. Suitable organic amines include lower-alkyl-substituted amines such as methylamine, dimethylamine, ethylamine, and trimethylamine, as well as ethanolamine, diethanolamine, triethanolamine, and substituted ethanolamines, typically lower alkyl-substituted ethanolamines such as N-methyl and N,N-dimethyl ethanolamines, and morpholine. Such compounds are also useful for bringing the pH into the desired range for basic formulations, and, if present, will generally represent not more than about 20 wt.% of the composition, and in most cases will represent not more than about 10 wt.% of the composition.

SUBSTRATES AND TREATMENT THEREOF:

The compositions and methods of the invention are generally applicable to a wide variety of substrates to improve the quality of images printed on the substrate surface. The substrates may be flexible or rigid, porous or nonporous, and cellulosic or noncellulosic. Suitable substrates with which the present compositions and methods can be used include, but are not limited to, textiles, paper, polymeric films, metallic sheets, and the like.

1. TREATMENT OF TEXTILE SUBSTRATES

Suitable textile substrates for use with the compositions and methods of the invention include textiles having natural, synthetic, cellulose-based, or non-cellulose-based fibers or any combination thereof. Exemplary textile substrates include, but are not limited to, textiles having hydroxy group-containing fibers such as natural or regenerated cellulosic fibers (cotton, rayon, and the like); nitrogen group-containing fibers such as

polyacrylonitrile; natural or synthetic polyamides (including wool, silk, or nylon); and/or fibers having acid-modified polyester and polyamide groups. The textile substrates may be additionally pre-treated or after-treated with resins or other substances compatible with the image-enhancing compositions and methods of the invention, and may be finished or
5 unfinished. The textile substrate may also be sized prior to application of the present image-enhancing compositions. Alternatively, the present image-enhancing compositions may be incorporated into an external sizing process and composition.

The fibers of the textile substrate may be in any suitable form compatible with the printing process to be used, *e.g.*, loose yarns, fabrics, and the like. Fabrics, however, are a
10 convenient and preferred form. The fibers may be blended with other fibers that are susceptible to treatment with a composition of the invention, or with fibers that may prove less susceptible to such treatment.

Treatment of textile substrates with the image-enhancing compositions of the invention can be carried out using any of a number of conventional textile coating and/or
15 treatment processes commonly employed in the art. In general, the image-enhancing composition is applied to the textile substrate to provide a treated textile substrate in a manner that leaves the image-enhancing agent physically and chemically accessible to inks for reaction of the colorant-reactive image enhancing agent within the colorant contained in the ink. The term "treatment" as used herein encompasses both surface coating and
20 infiltration of the textile to some degree, so long as, in the latter case, the image-enhancing agent is still accessible to colorant for printing.

The amount of image-enhancing composition applied to the textile substrate will vary with a number of factors, including the absorptive nature of the substrate, the ink to be used for printing, the printing method, and the like. In general, the image-enhancing
25 composition is applied in an amount representing approximately 0.5 wt.% to 20 wt.% of the textile substrate after drying. As will be appreciated by those skilled in the art, the compositions of the invention are applied by any suitable means, which may include continuous processes, application as a continuous film, padding, dipping, spraying, foam application, exhaust processes, or by using a rod, roll, flexopress, blade, or air-knife coater.

2. TREATMENT OF PAPER

The image-enhancing compositions of the invention can be used to treat a paper substrate, for example in a coating or sizing process. The term "paper" is meant to encompass a substrate based on cellulosic fibers; synthetic fibers such as polyamides, polyesters, polyethylene, and polyacrylic fibers; inorganic fibers such as asbestos, ceramic, and glass fibers; and any combination of cellulosic, synthetic, and inorganic fibers. Paper substrates that can be treated using the compositions of the invention may be of any dimension (*e.g.*, size or thickness) or form (*e.g.*, pulp, wet paper, dry paper, *etc.*). The paper may or may not have been sized prior to treatment according to the methods of the invention; that is, the present compositions can be applied to paper having either a pretreated surface or a surface that has not been treated or coated. The paper substrate is preferably in the form of a flat or sheet structure, which structure may be of variable dimensions. "Paper" is meant to encompass printing paper (*e.g.*, inkjet printing paper, *etc.*), writing paper, drawing paper, and the like, as well as board materials such as cardboard, poster board, Bristol board, and the like.

(A) PAPER COATING

The image-enhancing composition may be applied as a coating on sized paper either as a pretreatment (*i.e.*, prior to printing), simultaneously with printing, or as an after-treatment. As a paper coating, the compositions of the invention are applied to sized paper in quantities suitable to provide the desired characteristics of an image printed on the paper surface, including bleed resistance, water resistance (*e.g.*, water-fastness), *etc.* Typical amounts of image-enhancing composition to be applied as a top coating, on sized paper, generally range from about fifty (50) to about five hundred (500) pounds per ton of paper substrate, or about 2 to 30 g/m² (generally corresponding to a coating composition layer ranging in thickness from about several hundred Angstroms to several mils in thickness, typically in the range of approximately 100 Angstroms to 5 mm). Application of a coating in a selected thickness can readily be done by one of skill in the art using known techniques, for example, by varying the coating agent concentration and number of coatings and through selection of the application means.

For use as a paper coating composition, the image-enhancing composition of the invention is applied to any desirable paper substrate, usually to a type of pre-sized paper substrate commonly used in printing. Substrates for use in the invention may be comprised of cellulosic or non-cellulosic materials, and include, for example, substrates comprised of synthetic fibers such as polyamides, polyesters, polyethylene, and polyacrylic fibers; inorganic fibers such as asbestos, ceramic, and glass fibers, and combinations of cellulosic, synthetic, and inorganic fibers, with porous cellulose substrates being preferred. Preferred substrate for use herein is generally free cut sheet paper, with exemplary paper substrates including, but not limited to, copier grade paper, business card stock, resin-coated papers, cartons such as milk cartons and cardboard gift boxes.

Processes for coating pre-sized paper substrates are well known in the art, and can be performed either on-machine, as part of the initial paper manufacturing process, or off-machine, subsequent to completion of paper manufacture. Generally, coating is accomplished by dip coating, reverse roll coating, extrusion coating, saturation, and the like. However, where the image-enhancing composition is applied as a coating on-machine, in order to achieve acceptable manufacture speeds of about 100 to 3000 ft./per minute, it is recommended that the weight of the sized paper base be greater than 30 grams per square meter. When the final product is to exhibit gloss at a satisfactory level (generally greater than 50), the base sheet, before it receives the coating, should retard rapid drainage of the water or of the coating into the fibrous substrate.

(B) PAPER SIZING

The image-enhancing compositions of the invention can also be used to treat paper that has not been sized; in this embodiment, then, the compositions represent paper "sizing" compositions. The present image-enhancing compositions can be used in either an internal sizing process or in an external sizing process, although use in external sizing is preferred. "Internal sizing" involves introduction of a sizing composition at the pulp stage of paper manufacturing, resulting in the distribution of the composition within the fibrous mass subsequently used to produce a fibrous paper sheet. "External sizing" involves application of a sizing composition to a surface of a paper sheet, so that the sizing composition is present

on or in at least one of the two faces of the paper. External sizing also saturates the paper to various extents depending on the degree of internal sizing.

Exemplary external sizing techniques include, but are not necessarily limited, to, size press treatment, dip coating, reverse roll coating, extrusion coating, and the like. For example, the sizing composition can be applied with a size press by dip coating and can be applied by solvent extrusion. The size press can be a sheet-fed size press or a size press employing a continuous web, preferably a continuous web size press. Generally, in a sizing process, the image-enhancing compositions of the invention are applied in amounts ranging from about 10 to 500, preferably 30 to 500, pounds per ton of substrate.

10

3. OTHER SUBSTRATES

Other substrates that may be treated with the image-enhancing composition of the invention include, but are not limited to: polymeric substrates such as films, sheets, coatings, and solid blocks, comprised of, for example, polyesters (including "MYLAR" flexible film), vinyl polymers, polysulfones, polyurethanes, polyacrylates, polyimides, and the like; metallic substrates such as films, sheets, coatings, foils, and solid blocks, comprised of, for example, aluminum, brass, copper, or the like; inorganic substrates, particularly films, sheets, coatings, and solid blocks, comprised, of, for example, glass, metal oxides, silicon-containing ceramics, and the like; and laminates such as a paper/polymeric film or paper/metal foil laminate. It should be emphasized that the nature of the substrate is not critical; rather, it is the image-enhancing treatment of the invention that is key, as any substrate treated with the image-enhancing composition of the invention can be printed on to yield a high quality printed image.

15
20

25 METHOD FOR PROVIDING WATER-RESISTANT IMAGES ON TREATED SUBSTRATES:

The invention also features a method for providing a water-resistant (*e.g.*, water-fast) printed image on a substrate surface by first applying to the substrate surface an image-enhancing composition of the invention and then applying a colorant to the treated substrate, where the colorant contains reactive ionizable and/or nucleophilic groups capable of reacting

with the image-enhancing agent in the image-enhancing composition, i.e., the azetidinium polymer, the guanidine polymer, or the like.

In general, aqueous inks are used in the preparation of a printed image on the treated substrates of the invention. The aqueous ink may be any suitable ink having a
5 colorant, *e.g.*, a pigment, dye, or stain, having one or more reactive groups suitable for reacting, either covalently or ionically, with a colorant-reactive component of the image-enhancing agent present on the treated substrate. The selection of the specific ink and colorant will vary with the colorant-reactive component of the image-enhancing agent. For example, when the colorant-reactive component is an azetidinium group, the colorant
10 preferably has a nucleophilic group for reaction with the azetidinium group. Thus, preferred colorants for use in printing on a substrate having an azetidinium polymer in the applied image-enhancing composition are those containing one or more nucleophilic moieties, *e.g.*, an amino, carboxy, sulfonato, thiosulfonato, cyano, hydroxy or sulfido group or the like. Preferred colorants for use in printing on a substrate treated with a guanidine polymer are
15 those containing an anionic group, *e.g.*, having a carboxy, sulfonato, thiosulfonato, cyano, halo, or phosphonato group or the like.

The inks used in conjunction with the treated substrates of the invention may be inkjet inks. Water-soluble colorants in the inkjet ink may be acid dyes, direct dyes, basic dyes or dispersive dyes; preferred dyes are described in U.S. Patent Nos. 5,425,805,
20 5,537,137, and 5,441,561.

The selection of the aqueous based ink will depend upon the requirements of the specific application, such as desired surface tension, viscosity, drying time, the type of substrate upon which the ink is to be applied (printing medium), and the like. The aqueous liquid vehicle of inks suitable for use in the invention will generally be water, although other
25 nonorganic compounds which are either water soluble or water miscible may be included as well. The colorant may be dissolved, dispersed or suspended in the aqueous liquid vehicle, and is present in an amount effective to provide the dried ink with the desired color and color intensity.

In some instances, the dye is contained in a carrier medium composed of ink and a
30 water soluble organic solvent. For applications utilizing such a carrier medium,

representative solvents include polyols such as polyethylene alcohol, diethylene glycol, propylene glycol, and the like. Additional solvents are simple alcohols such as ethanol, isopropanol and benzyl alcohol, and glycol ethers, *e.g.*, ethylene glycol monomethyl ether, diethylene glycol monoethyl ether. Representative examples of water soluble organic
5 solvents are described in U.S. Patent Nos. 5,085,698 and 5,441,561.

Preferred colorants contained in the inks useful with the invention are dyes, including azo or "direct" dyes as well as dyes containing acidic groups (*e.g.*, carboxylate, phosphonate or sulfonate moieties), basic groups (*e.g.*, unsubstituted amines or amines substituted with 1 or 2 alkyl, typically lower alkyl, groups), or both. Specific examples of
10 suitable colorants include, but are not limited to, the following: Dispersol Blue Grains (Zeneca, Inc.), Duasyn Acid Blue (Hoechst Celanese), Duasyn Direct Turquoise Blue (Hoechst Celanese), Phthalocyanine blue (C.I. 74160), Diane blue (C.I. 21180), Pro-jet Cyan 1 (Zeneca, Inc.), Pro-jet Fast Cyan 2 (Zeneca, Inc.), Milori blue (an inorganic pigment equivalent to ultramarine) as cyan colorants; Dispersol Red D-B Grains (Zeneca, Inc.),
15 Brilliant carmine 6B (C.I. 15850), Pro-jet magenta 1 (Zeneca, Inc.), Pro-jet Fast magenta 2 (Zeneca, Inc.), Brilliant Red F3B-SF (Hoechst Celanese), Red 3B-SF (Hoechst Celanese), Acid Rhodamine (Hoechst Celanese), Quinacridone magenta (C.I. Pigment Red 122) and Thioindigo magenta (C.I. 73310) as magenta colorants; Dispersol Yellow D-7G 200 Grains (Zeneca, Inc.), Brilliant yellow (Hoechst Celanese), Pro-jet yellow 1 (Zeneca, Inc.), Pro-jet
20 Fast Yellow 2 (Zeneca, Inc.), benzidine yellow (C.I. 21090 and C.I. 21100) and Hansa Yellow (C.I. 11680) as yellow colorants; organic dyes; and black materials such as carbon black, charcoal and other forms of finely divided carbon, iron oxide, zinc oxide, titanium dioxide, and the like. Specific and preferred black colorants include Acid Black 48 (Aldrich), Direct Black 58756 A (Crompton & Knowles), BPI Molecular Catalytic Gray
25 (Brain Power), Fasday Cool Gray (Hunter Delator), Dispersol Navy XF Grains (Zeneca, Inc.), Dispersol Black CR-N Grains (Zeneca, Inc.), Dispersol Black XF Grains (Zeneca, Inc.), Disperse Black (BASF), Color Black FW18 (Degussa), Color Black FW200 (Degussa), Hostafine Black TS (Hoechst Celanese), Hostafine Black T (Hoechst Celanese), Duasyn Direct Black (Hoechst Celanese), Pro-jet Black 1 (Zeneca, Inc.) and Pro-jet Fast
30 Black 2 (Zeneca, Inc.).

PRINTED SUBSTRATES:

The invention also features a printed substrate produced using the methods and compositions described herein. The printed, treated substrate of the invention can be produced by any of a variety of printing techniques, including inkjet printing, laserjet printing, photocopying, and the like. In general, the printing process involves applying, in an imagewise pattern, an aqueous recording liquid to a substrate that has been treated with an image-enhancing composition of the invention. Inkjet printing processes are well known in the art; see, for example, U.S. Patent Nos. 4,601,777; 4,251,824; 4,410,899; 4,412,224; and 4,532,530.

Some substrates treated with the image-enhancing compositions of the invention, particularly paper substrates, can also be printed on using printing and/or copying processes that require dry or liquid electrophotographic-type developers, such as electrophotographic processes, ionographic process, and the like. The treated substrates of the invention can also be printed on using a process for generating images that involves generating an electrostatic latent image on an imaging member in an imaging apparatus, developing the latent image with a toner, and transferring the developed image to a treated substrate of the invention. Electrophotographic processes are known in the art; see, *e.g.*, U.S. Pat. No. 2,297,691. Ionographic and electrographic processes are also well known in the art; see, *e.g.*, U.S. Patent Nos. 3,611,419; 3,564,556; 4,240,084; 4,569,584; 2,919,171; 4,524,371; 4,619,515; 4,463,363; 4,254,424; 4,538,163; 4,409,604; 4,408,214; 4,365,549; 4,267,556; 4,160,257; and 4,155,093.

The treated substrates of the invention can also be printed on using a variety of other printing and imaging processes, such as offset printing, printing with pen plotters, handwriting with ink pens, and the like.

EXPERIMENTAL

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to prepare and use the compounds

-27-

disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C and pressure is at or near atmospheric.

5 Also, in these examples, unless otherwise stated, the abbreviations and terms employed have their generally accepted meanings. Abbreviations and tradenames are as follows (note that suppliers of each material are indicated as well):

Amres855 = azetidinium polymer (12.5% in water, Georgia Pacific);
Gum 280 = starch (Penford Gum 280, Penford);
10 HS30 = azetidinium polymer (30% in water, Georgia Pacific);
IPA = isopropyl alcohol
Jetcoat 20 = 25% calcium carbonate in water (Specialty Minerals);
Kymene = azetidinium polymer (Hercules);
PC, Polycup 172 = azetidinium polymer (Polycup);
15 Pollectron = styrene/poly(vinyl pyrrolidone) copolymer (Pollectron 430, ISP Technologies);
PVOH = polyvinyl alcohol (Airvol 523S, Air Products);
Sif = fumed silica (Aerosil MOX 170, Air Products);
Sip = precipitated silica (FK310, Degussa);
20 SMA = styrene-maleic anhydride copolymer (Georgia Pacific);
Surfinol S420 and F585 = surfactants (Air Products);
Surfinol DF66 = defoaming agent (Air Products);
Tinopal = brightener (Ciba Additives);
Vantocil = poly(iminoimidocarbonylhexamethylene hydrochloride, 20% aqueous
25 solution (Vantocil IB, Zeneca, Inc.);
W32 = leveling agent (Carboflow W32, B.F. Goodrich).

EXAMPLE 1: POLYAZETIDINIUM-BASED IMAGE-ENHANCING COMPOSITIONS

The following tables summarize exemplary image-enhancing compositions
30 prepared in accordance with the invention, wherein the image-enhancing agent is an azetidinium polymer.

TABLE I

Formulation No.	Amres855	PC	ISP937	GQ755	PVOH	IPA (ml)	W32 (ml)	Tinopal (mg)	NMP	Surfinol	Surfinol DF66
14b		5.5	2.0		2.5						
16a	7.0	2.0	1.0								
21a	4.0	6.0									
24b		8.0	1.0		1.0		.25	400			
27b		8.0	1.0		1.0						
30a		8.5	0.5		1.0						
34a		7.0		2.0	1.0						
38b		7.0		2.0	1.0	5	1			S 420/2ml	
45b		7.0		2.0	1.0				2	FS 85/2ml	
53c		6.0		2.0	2.0	2		50	1.75	FS 85/1.75ml	1-2 drops
54a		5.0		3.0	2.0	4		150	1.75	FS 85/1.75ml	1-2 drops
55c		7.0		2.0	1.0	4		250	1.75	FS 85/1.75ml	1-2 drops
57a		4.0		4.0	2.0	4		250	1.75	FS 85/1.75ml	1-2 drops
69b	4.0			4.0	2.0	4		250	1.75	FS 85/1.75ml	1-2 drops

TABLE 2
POLYAZETIDINIUM-BASED COMPOSITIONS

Formulation No.	Starch (Gum 280)	Azetidinium ("Amres")	Binder (PVOH)	Styrene/PVP ("Polectron")	Pigment 1:4 Sif:Sip	% Solids	Viscosity, cP	pH
84-1	53	20	7.0		20.0	14.5		
85-1	52.5	20	7.0		20.0	14.6		
74-2	22	38	8.0		32.0	13.3		
74-3	22	40	10.0		28.0	13.3	335	3.82
74-4	10	50	10.0		25.0	13.3		
79-1	13	50	11.0		26.0	16.3		3.75
71-2	22	36		9.4	32.8	25.3		3.74
76-1	22	38	6.0	2.0	32.0	13.3	348	3.73
76-2	22	36	6.0	4.0	32.0	13.3		
74-1	22	33	8.0	5.0	32.0	13.3	479	3.86
76-3	22	34	6.0	6.0	32.0	13.3	286	3.73
77-3	22	35	5.0	6.0	32.0	13.3		
77-2	22	34	5.0	7.0	32.0	13.3	250	3.73
72-2	22	33	5.0	8.0	32.0	23.1		3.74

TABLE 2, CONTINUED

Formulation No.	Starch (Gum 280)	Azetidinium ("Amres")	Binder (PVOH)	Styrene/PVP ("Pollectron")	Pigment 1:4 Sif:Sip	% Solids	Viscosity, cP	pH
78-2	22	33	5.0	8.0	32.0	14.1	667	4.0
77-4	22	38	10.0	10.0	20.0	13.1		3.79
79-2	35	10	10.0	10.0	35.0	18.8		4.10
77-1	27.5	47.5	12.5	12.5		10.8		3.75
78-1	22	33	5.0	8.0	32	15.4	182	6.70
90-1	23	30	10.0		35	14.5		
90-2	23	30	10.0		35	14.7		
90-3	23	30	10.0		35	13.4		
90-4	23	30	10.0		35	14.5		

EXAMPLE 2: POLYGUANIDINE-BASED IMAGE-ENHANCING COMPOSITIONS

The following table summarizes exemplary image-enhancing compositions in accordance with the invention, wherein the image-enhancing agent is a polyguanidine or an azetidinium polymer, or wherein the image-enhancing agent comprises a mixture of a
5 polyguanidine and an azetidinium polymer.

TABLE 3

Formulation No.	HS30	Amres855	VAN	PVOH	PC	Binder Polymer	Pigment	% Solids	Viscosity, cP
4-63-3		75.0					25 ¹	16.0	
4-57-4		0.0	25.0	25.0			50 ¹	20.0	
4-62-2		82.0	13.6	4.5				12.8	
4-62-1		64.2	10.7				25 ¹	16.2	
4-63-2		74.0	1.0				25 ¹	16.2	
5-90-5		50.0	3.0	10.0			35 ²	14.9	
5-92-1		45.0	4.0	10.0		4Pole	35 ²	15.5	
5-92-2		45.0	4.0	10.0		4Pole	35 ²	12.9	
4-81-2	74.0		1.0				25 ³	16.2	
4-83-1	72.0		1.0		2		25 ³	27.6	
4-84-1	72.0		1.0		2		25 ³	27.6	492
4-84-2	72.0		1.0		2		25 ³	23.0	265
4-85-1	72.0		1.0		2		25 ³	23.0	924

1: mixture of 1:4 Sif:Sip

2: mixture of 1:4 Sif:Sip and Jetcoat 20

3: Jetcoat 20

TABLE 4

Formulation No.	HS30	Amres855	ZrAc ₂	Vantocil	Poly172	Kymene	Jetcoat20	% Solids	Viscosity, cP
45-10	69.0			2.0	29.1				83
45-8	69.7			1.0	29.3				82
28-4	35.2		1.2		33.9		29.9	19.5	250
43-3	42.0		1.5			42.8	13.6		380
43-2	42.5		1.5			42.2	13.8		690
28-6	62.4		0.4		10.4		26.4	24.8	800
32-9		23.5	12.3		64.2		0.0		240
37-2		27.0	2.2		62.6		8.1		200
31-9		44.5	0.0		44.5		11.0		140
36-1		46.5	1.6		45.9		6.0		
34-2		46.5	1.5		46.1		6.0	14.0	500
28-5		55.4	0.7		21.2		22.7	14.3	130
35-2		55.4	1.4		34.2		5.3	13.0	160
43-1		98.5	1.5						>1000

TABLE 5
POLYGUANIDINE-BASED COMPOSITIONS

Formulation No.	Starch (Gum 280)	Azetidinium ("Amres")	Polyguanidine ("Vantocil")	Binder (PVOH)	Styrene/PVP ("Pollectron")	Pigment 1:4 Sif:Sip	Solids (%)	Tinopal	pH
46-2	45		17	10		28.0	14.2		
79-3	45		17	10		28.0	17.6		4.71
84-3	54	10	5	8		22.5	15.2		
84-2	60	10	5	5		20.0	14.8		
83-3	46	15	2	7		30.0	16.4		
83-2	40	20	3	7		30.0	16.5		
83-1	37	25	5	5		28.0	16.4		
73-1	10	50	5	10		25.0	24.0		3.94
73-2	35	5	5	10	10	35.0	18.1		4.40
88-1	50	10	5	5		30	14.5		6.61
88-2	50	10	5	5		30.0	14.5		6.62
89-3	25	10	10	5	5	40	16.2	5.0	

TABLE 5, CONTINUED

Formulation No.	Starch (Gum 280)	Azetidinium ("Amres")	Polyguanidine ("Vantocil")	Binder (PVOH)	Styrene/PVP ("Polectron")	Pigment 1:4 Sif:Sip	Solids (%)	Tinopal	pH
89-2	38	12.4	4.8	9.5	4.8	28.6	14.3	1.90	
88-3	55	10	5	5		23	14.0	2.0	
89-1	40	13	5	10		30	13.8	2.0	
51-5	60		40				12.5		
52-1	50		50				13.3		
55-2		71.4		14.3			6.0		
55-3		85.5		17.1			5.4		
51-4			25	25		50	20.0		
53-4		90	10				6.0		
53-1		73.7	26.3				4.8		
53-2		54.5	22.7	22.7			5.5		
54-4		71.4	14.3	14.3			6.6		
57-1		71	14	14			6.6		

EXAMPLE 3: EVALUATION OF THE IMAGE-ENHANCING COMPOSITIONS

Each of the representative formulations prepared in Examples 1 and 2 was effective to produce a coated paper substrate and a sized paper substrate having the beneficial features described herein, i.e., with respect to bleeding, wicking and water-fastness of an image printed on the paper surface using a water-based inkjet ink and an inkjet printer. The formulations were also evaluated on (1) aluminum foil and other metal foil sheets, (2) cotton and cotton/polyester blend textile materials, (3) resin-coated paper (i.e., PVC-coated paper), and (4) latex-saturated paper. Each of the aforementioned substrates was coated with a formulation set forth in Tables 1 through 5 using a knife, a Meyer rod, or rollers, to achieve a coating thickness in the range of about 2 g/m² to 30 g/m². After coating and drying, the treated substrates were printed on using a water-based inkjet ink. The printed images were found to be water-fast as well as bleed-resistant and rub-resistant, and of superior quality with respect to both optical density and brightness.

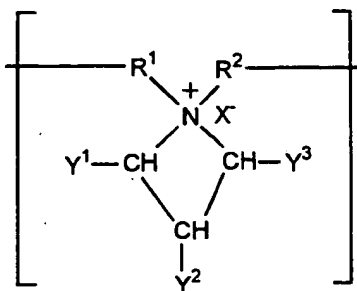
CLAIMS:

1. A process for treating a solid substrate, comprising applying to the surface of the substrate an image-enhancing composition comprised of an image-enhancing agent
 5 selected from the group consisting of (a) an azetidinium polymer, (b) a guanidine polymer, (c) a mixture of an azetidinium polymer and a guanidine polymer and (d) a copolymer of an azetidinium monomer and a guanidine monomer.

2. The process of claim 1, wherein the image-enhancing agent comprises an
 10 azetidinium polymer.

3. The process of claim 2, wherein the azetidinium polymer is comprised of monomer units having the structural formula

15



20

in which R^1 and R^2 are independently lower alkylene, X^- is an anionic, organic or inorganic counterion, and Y^1 , Y^2 and Y^3 are selected from the group consisting of hydrogen, hydroxyl, halo, alkoxy, alkyl, amino, carboxy, acetoxy, cyano and sulfhydryl.

25

4. The process of claim 1, wherein the image-enhancing agent comprises a guanidine polymer.

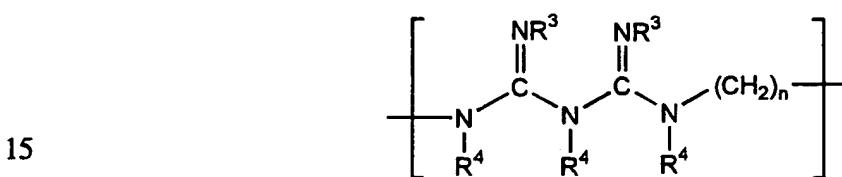
-38-

5. The process of claim 4, wherein the guanidine polymer is comprised of monomer units having the structural formula



wherein R³ is hydrogen or lower alkyl and R⁴ is hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy.

10 6. The process of claim 4, wherein the guanidine polymer is comprised of monomer units having the structural formula



wherein n is an integer in the range of 1 to 10 inclusive, R³ is hydrogen or lower alkyl and R⁴ is hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy.

20 7. The process of claim 1, wherein the image-enhancing agent comprises a mixture of an azetidinium polymer and a guanidine polymer.

8. The process of claim 1, wherein the image-enhancing agent is comprised of a copolymer of an azetidinium monomer unit and a guanidine monomer unit.

25

9. The process of claim 1, wherein the image-enhancing composition is aqueous.

10. The process of claim 1, wherein the image enhancing composition further includes up to about 40 wt.% of a film-forming binder.

30

-39-

11. The process of claim 10, wherein the film-forming binder represents approximately 1 wt.% to 25 wt.% of the image-enhancing composition after drying on a substrate.

5 12. The process of claim 11, wherein the film-forming binder represents approximately 1 wt.% to 15 wt.% of the image-enhancing composition after drying on a substrate.

10 13. The process of claim 10, wherein the film-forming binder is selected from the group consisting of polysaccharides, polypeptides, synthetic vinyl polymers, cationic film-forming binders, and derivatives thereof.

15 14. The process of claim 1, wherein the image-enhancing agent represents approximately 5 wt.% to 95 wt.% of the image-enhancing composition, based upon total solids weight of the composition after drying.

15. The process of claim 1, wherein the substrate is comprised of paper.

20 16. The process of claim 15, wherein the substrate is comprised of paper that has not been externally sized, and the image-enhancing composition is a sizing composition.

17. The process of claim 15, wherein the substrate is comprised of paper that has been externally sized, and the image-enhancing composition is a coating composition.

25 18. The process of claim 1, wherein the substrate is metallic.

19. The process of claim 1, wherein the substrate is comprised of an inorganic oxide.

30 20. The process of claim 1, wherein the substrate comprises a laminate.

-40-

21. A solid substrate treated with an image-enhancing composition comprised of an image-enhancing agent selected from the group consisting of (a) an azetidinium polymer, (b) a guanidine polymer, (c) a mixture of an azetidinium polymer and a guanidine polymer and (d) a copolymer of an azetidinium monomer and a guanidine monomer.

5

22. The treated substrate of claim 21, wherein the substrate is comprised of paper.

23. The treated substrate of claim 21, wherein the substrate is metallic.

10

24. The treated substrate of claim 21, wherein the substrate is comprised of an inorganic oxide.

25. The treated substrate of claim 21, wherein the substrate comprises a laminate.

15

26. A composition comprising an azetidinium polymer and a guanidine polymer.

27. A composition comprising a copolymer of an azetidinium monomer and a guanidine monomer.

20

28. A method for providing a water-resistant image on a substrate, comprising:
applying to the surface of a substrate an image-enhancing composition comprised of an image-enhancing agent selected from the group consisting of (a) an azetidinium polymer, (b) a guanidine polymer, (c) a mixture of an azetidinium polymer and a guanidine polymer, and (d) a copolymer of an azetidinium monomer and a guanidine monomer, to
25 provide a treated substrate; and

applying a dye composition to the treated substrate, wherein the dye composition contains a reactive dye having ionizable and/or nucleophilic groups capable of reacting with the image-enhancing agent.

30

29. A printed substrate prepared by the method of claim 28.

International Application No
PCT/US 99/08911

IPC 6 B41M1/26 B41M5/00 D21H17/54 D21H19/62 D21H21/16
C08L79/00 C08G73/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41M D21H C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 169 441 A (LAUZON RODRIGUE V) 8 December 1992 (1992-12-08) column 2, line 59 - column 3, line 62; claims 1,30; examples 1-7	1-9,14, 15,19, 21,22, 24,26,27
A	---	10-13,17
X	US 4 520 159 A (MASLANKA WILLIAM W) 28 May 1985 (1985-05-28) column 3, line 26 - column 4, line 24	1-5,7-9, 14,15, 21,22, 26,27
X	US 4 522 686 A (DUMAS DAVID H) 11 June 1985 (1985-06-11) the whole document	1-3,9, 14-16, 21,22

-/--

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

28 July 1999

Date of mailing of the international search report

05/08/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Nestby, K

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/08911

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 554 181 A (HILL LARRY O ET AL) 19 November 1985 (1985-11-19) the whole document, in particular example 6	1,4,5, 9-15,17, 21,22, 28,29
X	EP 0 286 597 A (SANDOZ AG ;COURTAULDS PLC (GB)) 12 October 1988 (1988-10-12) the whole document	1,4-6,9, 14,21, 28,29
X	US 4 718 918 A (HELLER JUERG ET AL) 12 January 1988 (1988-01-12) the whole document	1-3,9, 14,21, 28,29
X	DE 195 27 100 A (BAYER AG) 30 January 1997 (1997-01-30) the whole document	1,4,5,9, 14,15, 21,22, 28,29
A	US 5 525 664 A (MILLER ANDREW J ET AL) 11 June 1996 (1996-06-11) the whole document	1-3,7,9, 14,15, 21,22,26
A	US 5 712 027 A (ALI MAHFUZA B ET AL) 27 January 1998 (1998-01-27)	
A	US 5 659 011 A (WALDMANN JOHN J) 19 August 1997 (1997-08-19)	

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

PCT/US 99/08911

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5169441 A	08-12-1992	AT 124740 T	15-07-1995
		AU 642061 B	07-10-1993
		AU 8974291 A	18-06-1992
		CA 2057548 A	18-06-1992
		DE 69111034 D	10-08-1995
		DE 69111034 T	21-12-1995
		EP 0491346 A	24-06-1992
		ES 2076452 T	01-11-1995
		FI 915894 A	18-06-1992
		JP 4339867 A	26-11-1992
		MX 9102608 A	01-06-1992
US 4520159 A	28-05-1985	AT 43851 T	15-06-1989
		AU 569382 B	28-01-1988
		AU 4012585 A	26-09-1985
		BR 8501245 A	12-11-1985
		CA 1233594 A	01-03-1988
		EP 0156268 A	02-10-1985
		FI 851007 A,B,	22-09-1985
		JP 1897706 C	23-01-1995
		JP 6025256 B	06-04-1994
		JP 60212427 A	24-10-1985
US 4522686 A	11-06-1985	AT 23379 T	15-11-1986
		AU 551897 B	15-05-1986
		AU 8838282 A	24-03-1983
		BR 8205384 A	23-08-1983
		CA 1187658 A	28-05-1985
		DK 412282 A,B	16-03-1983
		EP 0074544 A	23-03-1983
		FI 823045 A,B,	16-03-1983
		JP 1627138 C	28-11-1991
		JP 2050240 B	01-11-1990
		JP 58060093 A	09-04-1983
		MX 166782 B	04-02-1993
		PH 18888 A	25-10-1985
		ZA 8206772 A	27-07-1983
US 4554181 A	19-11-1985	EP 0164196 A	11-12-1985
		JP 61010484 A	17-01-1986
EP 0286597 A	12-10-1988	AT 89621 T	15-06-1993
		AU 609460 B	02-05-1991
		AU 1415288 A	06-10-1988
		DE 3881095 A	24-06-1993
		DE 3881095 T	02-12-1993
		HK 49596 A	29-03-1996
		JP 63256777 A	24-10-1988
US 4718918 A	12-01-1988	CH 674786 A,B	31-07-1990
		DE 3446282 A	11-07-1985
		FR 2557602 A	05-07-1985
		GB 2154615 A,B	11-09-1985
		GB 2184739 A,B	01-07-1987
		JP 60155791 A	15-08-1985
		US 4599087 A	08-07-1986
DE 19527100 A	30-01-1997	NONE	

INTERNATIONAL SEARCH REPORT

information on patent family members

Int'l Application No

PCT/US 99/08911

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5525664 A	11-06-1996	NL 9302294 A	17-07-1995
		CA 2138891 A	01-07-1995
		DE 69400997 D	09-01-1997
		DE 69400997 T	07-05-1997
		EP 0662542 A	12-07-1995
US 5712027 A	27-01-1998	US 5589269 A	31-12-1996
		US 5342688 A	30-08-1996
		AU 6130894 A	26-09-1994
		AU 6406094 A	26-09-1994
		AU 6406194 A	26-09-1994
		CA 2155741 A	15-09-1994
		CA 2155846 A	15-09-1994
		CA 2156073 A	15-09-1994
		CN 1119003 A	20-03-1996
		CN 1119004 A	20-03-1996
		CN 1119005 A	20-03-1996
		DE 69403639 D	10-07-1997
		DE 69403639 T	15-01-1998
		DE 69403640 D	10-07-1997
		DE 69403640 T	15-01-1998
		DE 69411896 D	27-08-1998
		DE 69411896 T	01-04-1999
		EP 0688265 A	27-12-1995
		EP 0688266 A	27-12-1995
		EP 0688267 A	27-12-1995
		ES 2120613 T	01-11-1998
		JP 8508453 T	10-09-1996
		JP 8507729 T	20-08-1996
		JP 8507730 T	20-08-1996
		SG 48319 A	17-04-1998
		WO 9420304 A	15-09-1994
		WO 9420305 A	15-09-1994
		WO 9420306 A	15-09-1994
US 5659011 A	19-08-1997	CA 2148055 A	24-03-1996